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SOLIDIFICATION OF HIGHLY UNDERCOOLED LIQUID METALS AND ALLOYS. (U)

JAN 80 J H PEREPEZKO

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The undercooling and solidification of liquid alloys in fine droplet form has been examined by thermal analysis, X-ray diffraction and metallography. New maximum undercooling limits have been established for several metals and hypercooling has been demonstrated for the first time in a metallic system. In alloys some aspects of the phase selection kinetics for formation of metastable phases have been identified in eutectic, peritectic and monotectic reactions. The use of droplet samples allows the measurement of thermodynamic properties of under-		

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20. ABSTRACT (Continued)

cooled liquids and the study of microstructure development with changing undercooling. In some alloys, the effective isolation of nucleants that is possible with micron size droplets results in a continuous solidification to the amorphous state. The observations are presented in terms of the potential of undercooling for structure modification and rapid solidification technology.

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I. Introduction

During the period of project support from 8/15/76 to 8/14/79 research has been focused upon the formation of amorphous phases from liquid alloys at high undercooling and on several aspects of the undercooling and solidification of alloys. The experimental approach that has been adopted to carry out these studies involves the application of the droplet-emulsion technique. With this method samples may be produced which exhibit large undercoolings prior to solidification during slow cooling and which may be maintained in the metastable undercooled state for long time periods without the intervention of crystallization.

For some alloys, the large undercoolings that are attained in droplets permit the liquid to bypass crystallization and undergo a continuous vitrification to the amorphous state. With these alloys it has been possible to examine the undercooling conditions for vitrification and to elucidate the kinetic competition between crystal nucleation and amorphous phase formation at large undercoolings. In certain other alloys attention has been directed towards the determination of the maximum undercooling to crystallization and the reaction kinetics during important solidification reactions such as eutectic, peritectic and monotectic processes. Often the product structures that crystallize from the melt during these reactions have features which are distinct to high undercooling solidification. Several examples of metastable phase formation have been identified by thermal analysis and X-ray diffraction and a uniform microstructural morphology has been observed in some droplets indicating an absence of a heterogeneous dendritic crystallization.

II. Droplet-Emulsion Technique

In order to undercool a liquid metal to the maximum, the liquid must not contain nucleants nor can it be allowed to solidify in a container whose walls may catalyze nucleation. As a result, large samples of liquid are generally unsuitable for obtaining maximum undercooling since they almost inevitably contain extraneous nucleants. Instead, the most promising method of attaining maximum undercooling during nucleation is to utilize a collection of small isolated droplets. By starting with high purity materials and dispersing the liquid metal into a large number of small drops within a suitable carrier fluid only a few of the drops will contain potent nucleants. This is the principle of the droplet technique. If the droplets are kept separated by films that are not nucleation catalysts, then the effects of any nucleants can be restricted to the few drops in which they are located. When a sample

of liquid metal, in the form of an emulsion, is undercooled, the majority of the drops will not begin to solidify until the maximum undercooling temperature is reached. The growth rate of crystals from the liquid is very rapid at large undercooling. Hence, the formation of the first nucleus in any one drop will lead to rapid solidification of the entire drop. Since nucleation is the rate limiting step in the solidification of an undercooled liquid, the onset of exothermic crystallization in a differential thermal analysis record represents the nucleation temperature.⁽¹⁻³⁾ In addition, a fine droplet sample is well suited for phase identification analysis by X-ray diffraction.

III. Summary of Research Findings and Conclusions

The results of the current studies on droplet samples are of value in identifying some of the factors governing solidification at high undercooling and emphasize the importance of nucleation in determining the nature and distribution of phases following rapid solidification. The significance and implications of the observations are indicated in terms of the phase selection process. A consideration of the results not only demonstrates the unique potential of the droplet technique, but also provides a background for the further development of the application of the droplet technique to the solidification of undercooled liquid alloys. For most of the observations that are summarized in the following list a more detailed discussion along with a full and complete description of data has been presented in technical and progress reports, which have been submitted previously, and in literature publications. In addition, it is worthwhile to note that although the results that are presented involve observations on specific systems, it is believed that many of the findings have a general validity.

1) As a preliminary step to alloy solidification studies the droplet - emulsion technique has been applied to examine the maximum undercooling limit for several pure materials. Large undercooling values have been obtained for a number of pure metals, including Pb, Sn, In and Bi which exceed those reported in past studies⁽⁴⁻⁶⁾ by substantial amounts. A comparison of the present results with previous maximum undercooling values is presented in the list given in Table 1. The present results invalidate the correlation⁽⁴⁾ that the maximum undercooling is equivalent to $0.2T_m$ where T_m is the absolute melting temperature. This implies that similar large increases in maximum undercooling can be observed for other metals. In

addition to providing a basis for the study of alloy solidification, the new maximum undercooling values indicate a need to reconsider the estimates of σ_{LS} , the liquid-solid interfacial energy. An estimated value for σ_{LS} may be calculated from classical nucleation theory and the maximum undercooling.⁽²⁾ This calculation implies that $\sigma_{LS} \propto (\Delta T)^{2/3}$, so that the present undercooling limits require an increase of up to 50% in the value of σ_{LS} estimated from nucleation theory.

2) The large undercoolings that have been obtained in pure metals may be maintained in alloy droplet samples. There appears to be a general trend in alloys for the maximum undercooling nucleation temperature, T_n , to follow approximately the composition dependence of the liquidus phase boundary. However, there have been several observations of a departure from this trend when competing reaction modes are detected in the determination of T_n and phase selection at maximum undercooling.

3) In alloys, solidification by a eutectic or peritectic crystallization reaction may be suppressed at high undercooling by the intervention of a metastable solidification path. Several metastable paths have been identified and include the formation of phases with extended solid solubility, the nucleation of nonequilibrium intermediate alloy phases and the continuous solidification into an amorphous phase. These observations indicate that the interpretation of measurements of T_n , the maximum undercooling nucleation temperature, can be misleading unless diffraction studies and microstructural results are also considered.

4) In Sn-Bi alloys which form a simple eutectic system two forms of metastable solidification product reactions have been observed at high undercooling. For Sn-rich alloys, X-ray diffraction has confirmed that a fourfold metastable extension of primary solid solubility occurs up to almost the eutectic composition at 46 at/o Bi. At about the equiatomic composition equilibrium structure formation is bypassed entirely by the nucleation of an intermediate phase (SnBi). Although the SnBi phase is a nonequilibrium structure, it is sufficiently stable to thermal decomposition in droplet form so that its melting point, which is 30°C below the eutectic temperature, may be determined by DTA.

5) A detailed examination of the nucleation behavior in the Pb-Bi system during solidification at high undercooling has provided further evidence for the importance of metastable processes in the reaction kinetics. Under equil-

ilibrium conditions the Pb-Bi system displays both peritectic and eutectic solidification reactions. At high undercooling the peritectic reaction is bypassed by a $L \rightarrow \epsilon$ reaction and the eutectic reaction is replaced by either a $L \rightarrow \epsilon$ (supersaturated) or $L \rightarrow x$ reaction where x is a nonequilibrium intermediate alloy phase. In fact, the metastable nature of the solidification products is preserved even during heating. In this case the metastable ϵ phase is observed to melt by a direct $\epsilon \rightarrow L$ process in a superheated condition above the onset of equilibrium melting and the x phase undergoes a melting about 15°C below the eutectic isotherm at 125°C .

6) An examination of the phase selection kinetics in the Pb-Bi system has demonstrated the importance of undercooling in the formation of metastable phases. For example, a certain minimum level of undercooling is required to insure a favorable nucleation kinetics for the metastable x phase. At the same time, the amount of liquid undercooling is controlled to a large degree by the nature of the droplet surface coating which usually provides a site for the catalysis of solidification. The role of the droplet surface coating is emphasized by the observation that alternations in the nature of the coating can be used to generate either the metastable supersaturated ϵ phase or the metastable x phase in a given alloy. Both of these reactions can be induced to form at about the same T_n value, but at different undercooling values due to the difference in melting points of the ϵ and x phase. Modifications of the droplet surface coating can be effected by several methods including the use of different surfacant treatments⁽¹⁾ and the fact that the extent of coating film formation depends to some degree on the droplet size range.

7) In droplet dispersions of alloys in the Sn-Bi and Pb-Bi systems, metastable solidification products are sufficiently resistant to decomposition that they may be retained upon heating to allow for a determination of melting temperatures and metastable phase equilibria. There seems to be a relationship between the amount of undercooling to nucleation and the rate of solid state decomposition of metastable phases. Samples with coatings which yield a maximum undercooling tend to display sluggish decomposition kinetics and the highest decomposition temperatures.

8) The metastable intermediate phases that crystallize from the melt at high undercooling in the Bi-Sn and Pb-Bi systems are similar to structures which have been reported to become equilibrium phases under high pressure

conditions.^(7, 8) A similar analogy between the structure nucleated at high undercooling and that stabilized at high pressure⁽⁹⁾ has been observed in the nucleation of pure Bi and maximum undercooling. These observations suggest that phase structures which may be stabilized under elevated pressure conditions may compete successfully in the phase selection process involved in nucleation under normal pressure conditions in the highly undercooled state.

9) Some new features of the solidification of highly undercooled liquid alloys have been identified in thermodynamic measurements on a Pb-Bi eutectic alloy. It has been demonstrated for the first time in an alloy system that undercooling levels may be achieved which permit isenthalpic solidification. This condition may be described by the following relation:^(10, 11)

$$\Delta H_m(T_m) \leq \int_{T_n}^{T_m} C_p^l dT \quad (1)$$

where $\Delta H_m(T_m)$ is the heat of fusion at the melting point and allowance is made for a possible variation of the liquid specific heat, C_p^l , with undercooling to the nucleation temperature. The value of T_n which satisfies the equality given in Eq. (1) marks the onset of the hypercooled liquid regime. The specific heat and latent heat measurements of the Pb-Bi eutectic alloy point out two features which have not been widely recognized. First, the latent heat of solidification of an alloy may be appreciably less than that estimated from a weighted average of the pure components. This is especially true for eutectic reactions associated with steeply falling liquidus phase boundaries and is a consequence of the reduction in liquid enthalpy with decreasing temperature. Another point of significance is the observation that the latent heat of the x phase is about two-thirds of the latent heat for the equilibrium eutectic mixture. While this result is consistent with the metastable nature of the x phase, it indicates that the likelihood of attaining the hypercooled condition at a given level of undercooling can be enhanced considerably when the solidification yields a metastable product. Therefore, when the temperature and composition dependence of the terms in Eq. (1) are accounted for, it is apparent that the attainment of the hypercooled regime in alloys may be expected to be a common feature in highly undercooled liquids when metastable solidification products are possible.

10) In alloys, the occurrence of isenthalpic solidification of hypercooled liquids is often associated with the formation of a compositionally homogeneous product.^(12, 13) Observations of the microstructure developed in Pb-Sb alloys

following solidification at different levels of undercooling have confirmed this feature. At the same time the results of this investigation suggest that in practice solidification at high undercooling may deviate from the predictions of an adiabatic model that is commonly used to represent the onset of the hypercooling limit. For example, if significant heat transfer occurs during solidification, the enthalpy available for recalescence heating would be reduced and an effectively hypercooled condition would result at a lower undercooling than that predicted by an adiabatic model.

11) A key aspect in the progress of a monotectic solidification reaction is the separation of the initially homogeneous liquid into two liquid phases. In slowly cooled Bi-Ga droplet emulsions, clear evidence for a liquid phase separation has been obtained in DTA studies employing both heating and cooling traces. This information permits the identification of the locus of temperatures corresponding to an extension of the miscibility gap below the monotectic temperature. A subsidiary observation associated with these measurements concerns the amount of undercooling prior to the onset of phase separation. On the Bi-rich portion of the critical point in the monotectic miscibility gap noticeable undercooling has been detected, but on the Ga-rich portion no undercooling below the liquid phase boundary is observed before the onset of phase separation. These observations are in accord with a recent theory⁽¹⁴⁾ of the wetting characteristics of liquids involved in monotectic reactions and provide a first confirmation of critical point wetting in a metallic system.

12) The undercooling of a liquid droplet emulsion need not be terminated by the nucleation of a crystalline solid phase. The effective isolation of nucleant sites that is possible with droplet samples has allowed for the solidification of alloys near the eutectic composition in the Te-Cu system directly to the amorphous state during slow cooling. Thermal cycling DTA studies have identified the temperature range of viscosity controlled and nucleation controlled crystallization during cooling.

13) The composition dependence of T_n has been observed to provide a measure of the glass formation tendency as related to the kinetic competition between crystallization and vitrification at high undercooling. In the Te-Cu system, a significant lowering of T_n is manifested well before the composition range is encountered for easy glass formation.

14) In an initial study the compaction of loose amorphous powder has been achieved in a cold drawing operation. Observations of the fracture behavior of compacts have demonstrated that cold welding of droplets occurs during drawing provided the temperature is maintained below the glass transition.

Table 1

Maximum Undercooling Limits

<u>Metal</u>	<u>Undercooling (°C) (Previous Studies)</u>	<u>Reference</u>	<u>Undercooling (°C) (Current Work)</u>
Bismuth	90	4	227
Lead	80	4	153
Tin	110	4	184
Indium	-	-	110
Mercury	80	6	90
Tellurium	-	-	234

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Publications of the Current Research Program

During a research program, substantial time intervals often elapse between the completion of a research study, submission of a manuscript, and the final appearance of the paper in print. As a result, the following list gives publications in preparation as well as those in print or in press.

1. "Undercooling of Low-Melting Metals and Alloys," J. H. Perepezko, D. H. Rasmussen, I. E. Anderson and C. R. Loper, Jr., in Solidification and Casting of Metals, The Metals Society, London, 169 (1979).
2. "Discussion of Nucleation, Undercooling and Homogenous Structures in Rapidly Solidified Powders," J. H. Perepezko and D. H. Rasmussen, Met. Trans., 9A, 1490 (1978).
3. "Observation of Pure Quadrupole Resonance in Zinc Metal," E. N. Kaufman, J. R. Brookeman, P. C. Canepa, T. A. Scott, D. H. Rasmussen and J. H. Perepezko.[†]
4. "Solidification of Highly Undercooled Liquid Metals and Alloys," J. H. Perepezko, C. Galaup and D. H. Rasmussen, Proc. of 3rd European Symp. on Mat. Sci. in Space ESA SP-142, Paris, France, 375 (1979).^{††}
5. "Glass Formation and Crystallization in Highly Undercooled Te-Cu Alloys," J. H. Perepezko and J. S. Smith (to be submitted to Met. Trans.).
6. "Observations on the Metastability of Liquid Bi at High Undercooling," J. H. Perepezko, K. P. Cooper, I. E. Anderson and J. S. Paik (in preparation).
7. "The Peritectic Reaction in Undercooled Alloys," K. P. Cooper and J. H. Perepezko (in preparation).
8. "Metastable Solidification Products in Pb-Bi and Sn-Bi Alloys," I. E. Anderson, K. P. Cooper and J. H. Perepezko (in preparation).
9. "Crystallization of Undercooled Liquid Droplets," J. H. Perepezko (in preparation for Second International Conference on Rapid Solidification Processing: Principles and Technologies.)^{††}

[†]Based upon cooperative work with Dr. E. N. Kaufman and Bell Labs. This study demonstrates the high quality of metal samples prepared by the droplet emulsion technique.

^{††}Based upon a lecture presentation the Principal Investigator has been invited to deliver.

Technical Reports

1. Comprehensive Progress Report - Solidification of Highly Undercooled Liquid Metals and Alloys, August, 1977.

Presentations

1. "Solidification of Sn-Bi Alloys at High Undercooling," AIME Fall Meeting (1976).
2. "The Formation of an Amorphous Phase by a Slow Cooling from the Melt Technique," AIME Fall Meeting (1977).
3. "The Undercooling and Specific Heat of Liquid Metals," AIME Annual Meeting (1977).
4. "Solidification of Highly Undercooled Liquid Metals and Alloys," AIME Annual Meeting (1979).
5. "Metastable Solidification Products in Pb-Bi Alloys," AIME Fall Meeting (1979).

Patents

1. Compaction of Amorphous Metal Droplets Produced by Emulsification - Application number 960,100.

Participating Scientific Personnel

Professor J. H. Perepezko, Principal Investigator

Professor C. R. Loper, Jr., Co-Investigator

Dr. D. H. Rasmussen, Project Associate

Mr. I. Anderson, Graduate Student M.S. in 5/78, currently working on Ph.D.

Mr. J. Smith, Graduate Student M.S. work completed on 10/78, currently employed in industry in rapid solidification work

Mr. C. Galaup, Graduate Student, M.S. work to be completed on 5/80